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Claims

1. A method for controlling the thermal expansion behaviour of a material comprising the step of incorporating into the material a component including one

5   or more diatomic bridges, the or each bridge extending between two atoms in the component, characterised in that the or each diatomic bridge has at least one vibrational mode that causes the two atoms on either side of the bridge to be moved together to a similar or greater extent

10   than competing vibrational mode(s) that cause the two atoms on either side of the bridge to be moved apart.

2. A method as claimed in claim 1 wherein the component comprises a portion or the entirety of the material.

3. A method as claimed in claim 1 or 2 wherein the

15   component comprises a portion of the material in an amount or manner that predetermines the material thermal expansion behaviour.

4. A method as claimed in any one of the preceding claims wherein the diatomic bridge has at least two vibrational

20   modes δ_1 and δ_2 (as herein defined).

5. A method as claimed in any one of the preceding claims wherein the material comprises a plurality of diatomic bridges throughout an infinite molecular coordination network defining a lattice structure, such that changes in

25   lattice geometry induce material negative thermal expansion behaviour.

6. A method as claimed in any one of the preceding claims wherein the diatomic bridge is linear.

7. A method as claimed in any one of the preceding claims

30   wherein the diatomic bridge is defined by a linear cyanide -(CN)- bridge.

8. A method as claimed in any one of claims 1 to 4 wherein the diatomic bridge is defined by a carbon monoxide -(CO)- bridge, a di-nitrogen -(NN)- bridge, a nitrogen monoxide -(NO)- bridge or a carbide -(CC)- bridge.

9. A method as claimed in any one of the preceding claims wherein the component comprises a plurality of diatomic bridges and, for at least some of the diatomic bridges, the two atoms that are linked by the diatomic bridge are metals, semi-metals or non-metals.

10. A method as claimed in claim 9 wherein the two atoms on either side of the bridge are different atoms and thermal expansion is tuned by varying the relative ratios between two or more different atoms on either side of the diatomic bridge.

11. A method as claimed in claim 9 or 10 wherein the diatomic bridge is a cyanide ion coordinated to the metal or semi-metal atoms, and one or both metal or semi-metal atoms in turn coordinates one or more other cyanide ions, which in turn bridge to other atoms.

12. A method as claimed in claim 11 wherein each atom alternatively coordinates other ligands.

13. A method as claimed in claim 12 wherein the other ligands are uni- or multi-dentate, including water, alcohols, diols, thiols, oxalate, nitrate, nitrite, sulfate, phosphate, oxide, sulfide, thiocyanate, non-bridging cyanide, cyanate, nitrogen monoxide, carbon monoxide, dinitrogen.

14. A method as claimed in claim 13 wherein the material is an optionally desolvated salt.

15. A method as claimed in claim 13 or 14 wherein the component forms part of an assembly that is neutrally, positively or negatively charged.

16. A method as claimed in claim 15 wherein when the assembly carries a charge, counter-ions are incorporated within cavities within the assembly to provide neutrally charged materials.

17. A method as claimed in claim 16 wherein the counter-ions influence the thermal behaviour of the material, and counteract negative thermal expansion behaviour of the material.

18. A method as claimed in claims 16 or 17 wherein the material is porous.

19. A method as claimed in claim 18 wherein the counter-ions are included into pores of the material.

20. A method as claimed in any one of claims 16 to 19 wherein the counter-ions are varied either by ion exchange or synthetic modification, to vary the thermal behaviour of the material.

21. A method as claimed in any one of claims 13 to 20 wherein the material comprises guest molecules located in interstitial cavities within a lattice thereof.

22. A method as claimed in claim 21 wherein the guest molecules influence the thermal behaviour and optionally counteract negative thermal expansion behaviour of the material.

23. A method as claimed in claim 21 or 22 wherein the material is porous and the guest molecules are located in pores of the material.

24. A method as claimed in any one of claims 21 to 23 wherein the guest molecules are varied either by sorption/desorption or synthetic modification, to vary the thermal behaviour of the material.

25. A method as claimed in any one of claims 21 to 24 wherein the guest molecules comprise one of more of water, alcohols, organic solvents or gas molecules.

26. A method as claimed in any one of claims 13 to 25
wherein the material has a topology based on a diamond-,
wurzite-, quartz-, cubic-, (4,4)-, (6,3)-, (10,3)-, PtS-,
NbO-, Ge_3N_4-, $ThSiO_2$- or PtO_x-type net.

5   27. A method as claimed in claim 26 wherein the material
comprises more than one interpenetrating net of the same
or different topology.

28. A method as claimed in any one of the preceding claims
wherein the material comprises zero-dimensional bridged

10   moieties, such as CN bridged molecular squares.

29. A method for controlling the thermal expansion
behaviour of a material comprising the step of
incorporating into the material a component including one
or more multi-atomic bridges, the or each bridge extending

15   between two atoms in the material, characterised in that
the or each multi-atomic bridge has at least one
vibrational mode that causes the two atoms on either side
of the bridge to be moved together to a similar or greater
extent than competing vibrational mode(s) that cause the

20   two atoms on either side of the bridge to be moved apart.

30. A method as claimed in claim 29 wherein the component
comprises diatomic bridges as defined in any one of claims
4 to 13, or polyatomic bridges such as cyanamide,
dicyanamide, tricyanomethanide, thiocyanate,

25   selenocyanate, cyanate, isothiocyanate, isoselenocyanate,
isocyanate, azide, cyanogen or butadyinide.

31. A method as claimed in claims 29 or 30 that is
otherwise as defined in any one of claims 1 to 28.

32. A method for controlling the thermal expansion

30   behaviour of a material comprising the step of
incorporating into the material a component that has a
coefficient of thermal expansion less than $-9 \times 10^{-6} \, K^{-1}$.

33. A method as claimed in claim 32 wherein the component has a coefficient of thermal expansion that ranges from:

$-9 \times 10^{-6} K^{-1}$ to $-21 \times 10^{-6} K^{-1}$ in all directions; or

$-15 \times 10^{-6} K^{-1}$ to $-62 \times 10^{-6} K^{-1}$ along any one direction.

34. A method as claimed in claim 32 or 33 that is otherwise as defined in any one of claims 1 to 30.

35. A method for altering the thermal expansion behaviour of a material that comprises a component having a plurality of diatomic bridges, each bridge extending between two atoms in the component and having at least one vibrational mode that causes the two atoms on either side of the bridge to be moved together to a similar or greater extent than competing vibrational mode(s) that cause the two atoms on either side of the bridge to be moved apart, the method comprising the step of incorporating into the component two or more different atoms such that, for at least some of the diatomic bridges, the two atoms on either side of the bridge are different.

36. A method as claimed in claim 35 wherein the thermal expansion is tunable by varying the relative ratios between the two or more different atoms on either side of the diatomic bridge.

37. A method as claimed in claim 35 or 36 wherein the two atoms on either side of the bridge are different metals, semi-metals or non-metals, or combinations thereof.

38. A method for controlling the thermal expansion behaviour of a material substantially as herein described with reference to the Examples and/or the accompanying drawings.

39. A material having a thermal expansion behaviour controlled by the method of any one of the preceding claims.

40. A material as claimed in claim 39 comprising one or more of:

(a) materials based on the $Zn(CN)_2$-type or $2x(6,4)$ cubic structure (doubly interpenetrating diamond nets), optionally including substitution of divalent metals for some or all of the Zn atoms, including Cd(II), Hg(II),

5   Mn(II), Be(II), Mg(II), Pb(II) and Co(II), and optionally comprising substitution of mixtures of univalent, and optionally divalent and trivalent metal ions for Zn to give materials of the form:

$$\{ (M1_i^{II})_n (M1_j^{II})_{x2...} (M1_a^{II})_m \}\{ (M2_i^{I}) (M3_j^{III}) \}_{y1}\{ (M2_j^{I}) (M3_j^{III}) \}_{y2...}$$

10   $\{ (M2_a^{I}) (M3_a^{III}) \}_{ym}(CN)_2$ where $M1_i$ includes Zn(II), Cd(II), Hg(II), Mn(II), Be(II), Mg(II), Pb(II) and Co(II); $M2_i$ includes Li(I) and Cu(I); $M3_k$ includes Al(III), Ga(III) and In(III); n and m being any non-negative whole numbers with at least one greater than or equal to unity; and $(x1 + x2$

15   $+... +xn) + 2 x (y1 + y2 +... +ym) = 1$; and i, j and k being any positive integer;

(b) materials of (a) but with a single diamond-type network rather than two interpenetrating networks, optionally with other ions or molecules incorporated into

20   the structure, optionally with the inclusion of lower- or higher-valent metals into the network lattice;

(c) materials of (a) and (b) but with more than two interpenetrating diamond networks;

(d) materials based on $Ga(CN)_3$-type structure, optionally

25   satisfying the general formula:

$$\{ (M1_i^{III})_n (M1_j^{III})_{x2...} (M1_a^{III})_m \}\{ (M2_i^{II}) (M3_j^{IV}) \}_{y1}\{ (M2_j^{II}) (M3_j^{IV}) \}_{y2...}\{ ($$
$M2_a^{II}) (M3_a^{IV}) \}_{ym}(CN)_3$ where M1 includes trivalent metal ions including Fe(III), Co(III), Cr(III), Ti(III), Al(III), Ir(III), Ga(III), In(III) and Sc(III); M2 includes

30   divalent metal ions including Mg(II), Zn(II), Cd(II), Co(II), Fe(II), Ru(II), Mn(II) and Ni(II); M3 includes tetravalent metal ions such as Pd(IV) and Pt(IV); n and m being non-negative whole numbers with at least one greater

than or equal to unity; and $(x1 + x2 + ... + xn) + 2 \times (y1 + y2 + ... + ym) = 1$;

(e) materials of (d) but with other ions or molecules being incorporated in the structure, including lower- or higher-valent metals in the network lattice;

(f) materials of (d) to (e) but with more than one interpenetrating cubic framework;

(g) other simple metal cyanides not explicitly belonging to (a) to (f) of the general form:

$(M1^{n1+})_{x1}(M2^{n2+})_{x2}...(Mk^{nk+})_{xk}(CN)_i(.\{guest\})$ where M1, M2 ... Mk were metals with oxidation states n1+, n2+ ... nk+ respectively; k and i were positive whole numbers; $(x1 \times n1) + (x2 \times n2) + ... + (xk \times nk) = i$; and {guest}, when present, includes any solvent or molecular species such as water, alcohols, organic solvents or gas molecules, optionally including single or multiple interpenetrating regular nets including quartz, NbO, PtS, Ge_3N_4, (10,3), $ThSiO_2$, PtO_x or wurtzite nets;

(h) materials of (g) but with other ions or molecules incorporated into the structure, including lower- or higher-valent metals in the network lattice;

(i) materials other than (h) comprising more than one type of network lattice;

(j) materials as in (a) to (i) but with metal and/or cyanide vacancies within the structure;

(k) materials other than (a) to (j) comprising cyanide-bridged atoms, including cyanide-bridged materials in which the coordination spheres of some or all metal atoms include one or more non-cyanide bridges, including water, alcohols, diols, thiols, oxalate, nitrate, nitrite, sulfate, phosphate, oxide, sulfide, thiocyanate, (non-bridging) cyanide, cyanate, nitrogen monoxide, carbon monoxide or dinitrogen, optionally comprising regular

nets, and optionally including interstitial ions or guest molecules;

(l) materials of (k) that comprise finite cyanide-bridged moieties, optionally comprising cyanide-bridged polyhedra, polygons or finite chains, optionally comprising branches and components unrelated or unconnected to the cyanide-bridged moieties;

(m) materials of (a) to (l) where chemical composition is varied within the one crystal/crystallite by variation of crystallisation conditions, including concentrations and temperatures during crystallisation;

(n) materials of (a) to (l) where structure type, guest inclusion or ion inclusion is varied within the one crystal/crystallite; and

(o) amorphous materials or glasses based on any one of (a) to (n).

41. A material as claimed in claim 40 wherein:

* material (a) comprises $Zn(CN)_2$, $Zn_{0.8}Cd_{0.2}(CN)_2$, $Zn_{0.64}Cd_{0.36}(CN)_2$, $Cd(CN)_2$, $Mn(CN)_2$, $Zn_{0.5}Hg_{0.5}(CN)_2$, $Li_{0.5}Ga_{0.5}(CN)_2$ and $Cu_{0.5}Al_{0.5}(CN)_2$;

* material (b) comprises $Cd(CN)_2.\frac{1}{2}CCl_4$, $[NMe_4]_{0.5}[Cu^I_{0.5}Zn^{II}_{0.5}(CN)_2]$, $Cd(CN)_2.CMe_4$, $Cd(CN)_2.CMe_3Cl$, $Cd(CN)_2.CMe_2Cl_2$, $Cd(CN)_2.CMeCl_3$, $Cd(CN)_2.CCl_4$, $Cd_{0.5}Hg_{0.5}(CN)_2.CCl_4$, $Cd_{0.5}Zn_{0.5}(CN)_2.CCl_4$;

* material (d) comprises $Ga^{III}(CN)_3$, $Co^{III}(CN)_3$, $Al^{III}(CN)_3$, $Cd^{II}_{0.5}Pt^{IV}_{0.5}(CN)_3$ and $Zn^{II}_{0.5}Pt^{IV}_{0.5}(CN)_3.$;

* material (e) comprises the Prussian blues compounds such as $K[Fe^{II}Fe^{III}(CN)_6]$, and their analogues such as $Cs_2[Li^IFe^{III}(CN)_6]$, $Cd^{II}_{0.5}Pt^{IV}_{0.5}(CN)_3.H_2O$, $Zn^{II}_{0.5}Pt^{IV}_{0.5}(CN)_3.H_2O$, $K[Fe^{II}Fe^{III}(CN)_6].xH_2O$);

* material (g) comprises Ag^ICN, Au^ICN, $Zn^{II}Ag^I_2(CN)_4$, $Zn^{II}Au^I_2(CN)_4$;

* material (h) comprises $KCd^{II}[Ag^I(CN)_2]_3$ and $KCd^{II}[Au^I(CN)_2]_3$;

* material (i) comprises $Zn^{II}Ag^{I}_2(CN)_4 \cdot 0.575Ag^{I}CN$;

* material (j) comprises $Mn^{II}Co^{III}_{0.33}Cr^{III}_{0.33}(CN)_4$,

$Cd^{II}Fe^{III}_{0.33}Co^{III}_{0.33}(CN)_4$, $Cd^{II}Co^{II}_{0.33}Ir^{II}_{0.33}(CN)_4$, $Pd^{II}Cr^{II}_{0.33}Ir^{II}_{0.33}(CN)_4$ and $Cu^{II}Co^{III}_{0.66}(CN)_4$;

5 * material (k) comprises $Ni^{II}(CN)_2 \cdot xH_2O$,

$Fe_4[Re_6Se_8(CN)_6]_3 \cdot 36H_2O$, $Cd^{II}Ni^{II}(CN)_4 \cdot xH_2O$ and $Cd^{II}Pt^{II}(CN)_4 \cdot xH_2O$; and

* material (m) comprises $Zn_xCd_{1-x}(CN)_2$.

42. A material that comprises a component having a

10 plurality of diatomic bridges, each bridge extending

between two atoms in the component and having at least one

vibrational mode that causes the two atoms on either side

of the bridge to be moved together to a similar or greater

extent than competing vibrational mode(s) that cause the

15 two atoms on either side of the bridge to be moved apart,

wherein, for at least some of the diatomic bridges, the

two atoms on either side of the bridge are different.

43. A material as claimed in claim 42 wherein the two

atoms on either side of the bridge are different metals,

20 semi-metals or non-metals, or combinations thereof.

44. A composite incorporating a material as claimed in any

one of claims 40 to 43 or incorporating a material

produced by the method of any one of claims 1 to 38.

45. A composite as claimed in claim 44 comprising two or

25 more different materials, at least one of which is

produced by the method of any one of the claims 1 to 38.

46. A composite as claimed in claim 45 further comprising

a binding agent for the two or more different materials.

47. A composite as claimed in claim 45 including a

30 material produced by the method of any one of the claims 1

to 38 together with an unrelated material (as herein

defined).

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48. A composite as claimed in claim 47 further comprising a binding agent for the material and unrelated material.

49. A device formed from or comprising material having controllable thermal expansion behaviour, the material

5   being produced by a method as claimed in any one of claims 1 to 38, or being as claimed in any one of claims 40 to 48.

50. A device as claimed in claim 49 that is: an optical fibre; a laser; an optical, electronics or thermal

10   electronics component; a substrate or support for an optical component, electronics device or thermal electronics device; a thermal transfer device; a zero insertion force socket; a component for a superconductor, high precision instrument or frequency resonator; an

15   optical device displaying birefringence or that is optically transparent; an interference device; or a device that displays: piezoelectric properties; optical activity; or nonlinear optical properties.

51. A method for directing the thermal expansion behaviour

20   of a material comprising the step of incorporating into the material a component including one or more diatomic bridges, the or each bridge extending between two atoms in the component, with the or each diatomic bridge having at least one vibrational mode that causes the two atoms on

25   either side of the bridge to be moved together to a similar or greater extent than competing vibrational mode(s) that cause the two atoms on either side of the bridge to be moved apart, characterised in that the component comprises an anisotropic single crystal that, by

30   virtue of its alignment in the material, directs thermal expansion.

52. A material having directed thermal expansion
behaviour, the material being produced by the method of
claim 51.

53. A method as claimed in claim 51 or a material as
claimed in claim 52 wherein the component comprises a
portion or the entirety of the material.